Remediation Division

PETROLEUM RELEASE SECTION

Technical Guidance Document #8

Laboratory Analytical Requirements for Petroleum Releases Regulated by the Petroleum Release Section

The Department of Environmental Quality (DEQ) Petroleum Release Section (PRS) has changed its requirements regarding analytical laboratories and analytical methods. Three primary areas of concern are addressed below: 1) Volatile Petroleum Hydrocarbon (VPH) analysis, 2) Extractable Petroleum Hydrocarbons (EPH) analysis, and 3) the criteria for inclusion on the Petroleum Release Section laboratory list.

The DEQ PRS is in the process of implementing Risk-Based Corrective Action for evaluating health and environmental risks at site where there have been releases or spills of petroleum hydrocarbons. As a result, the DEQ has switched from GRO/DRO to analytical methods (VPH/EPH) which better characterize the composition and environmental behavior of the contaminant and allow for making more thorough evaluations of the contaminant's health and environmental risks.

The VPH and EPH methods were developed by the Massachusetts Department of Environmental Protection (MADEP). Copies of these methods are available through the Montana DEQ PRS.

Volatile Petroleum Hydrocarbons

The DEQ has required the use of the Volatile Petroleum Hydrocarbon Method (VPH) for analysis of soil and groundwater samples submitted to analytical laboratories since October 15, 1999. The VPH method replaces GRO/MBTEX for all samples collected from a site where a release or a suspected release of gasoline, jet fuel JP-4, mineral spirits, stoddard solvent, aviation gas or other similar petroleum product has or is thought to have occurred.

Second Column or Second Method Confirmation of MTBE and Naphthalene

Second Column or Second Method confirmation of MTBE and Naphthalene is required for all soil samples that have concentrations of MTBE and Naphthalene that are greater than one-half of the default Risk-Based Corrective Action (RBCA) Tier 1 risk-based screening levels (RBSLs). The default RBSLs are 0.1 mg/kg for MTBE and 9 mg/kg for Naphthalene.

Second Column or Second Method confirmation of MTBE and Naphthalene is required for all groundwater samples that have concentrations of MTBE and Naphthalene that are greater than one-half of the Human Health Standard (HHS). The HHS is 30 ug/l MTBE and 100 ug/l for Naphthalene.

Extractable Petroleum Hydrocarbons

The DEQ has required the use of the Extractable Petroleum Hydrocarbon Method (EPH) for analysis of soil and groundwater samples submitted to analytical laboratories since October 15, 1999. The EPH method replaces DRO for all samples collected from a site where a release or a suspected release of diesel #1, diesel #2, jet-A, kerosene, waste oil, heating (fuel) oil #3-6, mineral/dielectric fluids or other similar petroleum product has or is thought to have occurred. Additional testing is required for soil samples with total extractable hydrocarbon (TEH) concentrations exceeding the EPH screening level of 50 parts per million (ppm) (see EPH Screen below). If required, groundwater samples will be tested for MBTEXN and aliphatic and aromatic fractions by the VPH Method regardless of the EPH screen results.

EPH Screen

The DEQ is using screening technique that is outlined in the EPH Method to evaluate soils at diesel release sites. The screening technique is similar to a DRO analysis and generates a TEH concentration.

EPH Screen – Soils

A **TEH concentration of 50 ppm** has been selected for the screening action level for soil samples. If the screening TEH concentration is 50 ppm or less, then no additional analytical work is required. If the screening result is greater than 50 ppm, then the sample will be subjected to the EPH fractionation step plus VPH analysis for the aromatic and aliphatic fractions plus MTBE, BTEX and Naphthalene and on a case by case basis, PAH analysis. PAH analysis for soils will be performed via the EPH analysis.

EPH Screen – Groundwater

A TEH concentration of 300 parts per billion (ppb) has been selected as the screening level for groundwater. . If the TEH concentration is greater than 300 ppb then additional EPH analysis may be required. EPA Method 8270 will be used for PAH analysis for groundwater samples.

The decision for requiring EPH fraction data and/or PAH analysis by EPA Method 8270 will be a site-specific determination.

Definitions of Reported Values and Method Standards

The Montana PRS requires that the laboratories provide concentrations of three fractions for VPH analysis along with the target compounds. For VPH, concentrations of C5-C8 aliphatics, C9-C12 alphatics and C9-C10 aromatics are to be reported along with concentrations of MTBE, benzene, toluene, ethylbenzene, xylenes and naphthalene.

VPH concentrations are defined as the collective fractions of hydrocarbon compounds eluting from n-pentane to naphthalene, excluding target VPH analytes. C5-C8 aliphatics are defined as all hydrocarbons eluting on the FID chromatogram from n-pentane (C5) to just before n-nonane (C9). C9-C12 aliphatics are defined as all hydrocarbon compounds that elute on the FID chromatogram from n-nonane (C9) to just before naphthalene. C9-C10 aromatics are defined as all hydrocarbon compounds that elute on the PID chromatogram from just after o-xylene to just before naphthalene. These definitions are further defined in the method.

For EPH, when contaminant concentrations in soil samples exceed 50 ppm TEH, concentrations of the C9-C18 aliphatic, C19-C36 aliphatic and C11-C22 aromatic fractions and target compounds MTBE, benzene, toluene, ethylbenzene, xylenes and naphthalene are to be reported. On a case by case basis, target PAH analytes will also be reported.

EPH is defined as the collective fractions of hydrocarbon compounds eluting from n-nonoane to n-hexatriacontane, excluding Target PAH analytes. C9-C18 aliphatics are defined as all aliphatic hydrocarbon compounds eluting from n-nonane (n-C9) to just before n-nonadecane (n-C19). C19-C36 alphatics are defined as all aliphatic hydrocarbon compounds eluting from n-nonadecane (n-C19) through n-hexatriacontane (n-C36). C11-C22 aromatics are defined as all aromatic hydrocarbons eluting from naphthalene through Benzo(g,h,i)Perylene, excluding Target PAH analytes. These definitions are further defined in the method.

<u>Analytical Requirements for Volatile Petroleum Hydrocarbons and Extractable Petroleum</u> Hydrocarbons in Soil

Tables 1 and 2 below outline the analytical methods that are recommended for individual petroleum products. For example, in Table 1, the EPH screen is required for the initial soil analysis for diesel #2. If the EPH screen result TEH concentration is greater than 50 ppm, then further analytical work is required. The VPH method will be run to determine the concentrations of MTBE, benzene, toluene, ethylbenzene, xylenes and naphthalene (MBTEXN) and the C5-C8 aliphatic, C9-C12 aliphatic and C9-C10 aromatic fractions that are present in the soil and the C9-C18 aliphatic, C19-C36 aliphatic and C11-C22 aromatic fractions will be obtained using the EPH fractionation step.

Table 1- Testing Procedures for Soils

Pable 1- Testing Proc			EPH	EPH for
Petroleum Product		EPH Screen	Fractionation	PAHs
	VPH			
Gasoline	R			
Diesel #1	X	R	X	
Diesel #2	X	R	X	
#3- #6 Fuel Oils		R	X	
Waste Oil	X	R	X	SS
Jet Fuel/Kerosene		R	X	
Mineral/Dielectric		R	X	
Oils				
Heavier Wastes		R	X	X
Crude Oil	R	R	X	X
Unknown	R	R	X	SS
Oils/Sources				

R- required analysis

 $X\,$ - analysis to be run if the EPH screen concentration is >50 ppm TEH

SS- Site specific determination. Analysis may be required if the EPH screen concentration is >50 ppm TEH.

Analytical Requirements for Volatile Petroleum Hydrocarbon and Extractable Petroleum Hydrocarbons in Groundwater

VPH analysis is required for all products that may contain volatile organic compounds. For diesel sites the EPH screening technique will be used to generate a TEH concentration. If the TEH concentration is greater than 300 ppb then additional EPH analysis may be required. The decision for requiring EPH fraction data and/or PAH analysis by EPA Method 8270 will be a site-specific determination.

Table 2 - Testing Procedures for Groundwater

	VPH	EPH	ЕРН	EPA Method
Petroleum Product		Screen	Fractions	8270 for PAHs
Gasoline	R			
Diesel #1	R	R	SS	SS
Diesel #2	R	R	SS	SS
#3- #6 Fuel Oils		R	SS	SS
Waste Oil	R	R	SS	SS
Jet Fuel/Kerosene	R	R	SS	SS
Mineral/Dielectric		R	SS	SS
Oils				
Heavier Wastes		R	SS	SS
Crude Oils	R	R	SS	SS
Unknown	R	R	SS	SS
Oils/Sources				

R - required analysis

SS – Site-Specific determination. Analysis may be required if the EPH screen concentration is >300 ppb TEH.

Volatile Petroleum Hydrocarbon Soil Preservation

The VPH method calls for methanol preservation with 2- 40 ml. glass vials containing preweighed amounts of methanol. At this point in time the DEQ is not requiring methanol preservation. The 4 ounce jar included with the methanol preserved samples is for a moisture analysis, which is a requirement of the VPH method.

Reporting Requirements

Level III quality assurance information must be supplies with each analysis.

The minimum data package for VPH analysis must include the following: Results Summary Report Including PID and FID Surrogate Recovery Data PID and FID chromatograms Continuing Calibration Verification Reports

Laboratory Method Blank Reports

Laboratory Fortified Blank Reports

Duplicate Analysis or Matrix Spike/Matrix Spike Duplicate analysis reports

Chain of Custody Form(s)

Sample Receipt Checklist.

The minimum data package for EPH analysis must include the following:
Results Summary Report Including Surrogate Recovery Data
Aliphatic and Aromatic Chromatograms
Continuing Calibration Verification Reports
Laboratory Method Blank Reports
Laboratory Fortified Blank Reports
Duplicate Analysis or Matrix Spike/Matrix Spike Duplicate analysis reports
Chain of Custody Form(s)
Sample Receipt Checklist.

Criteria for Inclusion on the Petroleum Release Section laboratory Approval list

The Petroleum Release Section laboratory list only includes laboratories that have supplied the following documents for review:

- Quality Assurance Plan
- List of all equipment used
- List of all analyses performed
- Current Price List
- List of the Qualifications and positions of all employees
- Example VPH and EPH reports for samples containing measurable concentrations of gasoline and diesel respectively. Be sure to include the data package for each report.

Updated fee schedules, equipment lists, etc. must be supplied to the Petroleum Release Section when changes occur.

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